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2,931,759

SOLDERABILITY OF TIN PLATE

Uno T. Hill, Gary, Ind., assignor to Inland Steel Company, Chicago, Ill., a corporation of Delaware

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This invention relates to improvements in the manufacture of tin plate and more particularly to a method of improving the solderability characteristics of differentially coated tin plate.

The production of tin plate by continuous electrolytic tinning involves the steps of passing a ribbon or strip of steel through a tank containing a solution of a tin salt and therein electrodepositing tin on the steel strip. After leaving the tinning tank, the freshly plated strip passes through a furnace or oven at a temperature sufficiently high to fuse the tin in order to form a bright even coating on the steel strip, the latter step being known as flow brightening. A more recent development in electrolytic tinning is the production of differentially coated tin plate wherein the electrolytic tinning step is so regulated that one side of the steel strip receives a relatively heavy coating of tin and the other side receives a relatively lower weight coating of tin. For purposes of manufacturing tin cans and the like, a relatively heavy, corrosion resistant coating of tin is required only on the inside of the can. Thus, the use of differentially coated tin plate avoids an unnecessarily heavy external coating of tin thereby resulting in important economies in the use of tin.

However, with the advent of differentially coated tin plate in the industry, it was necessary that the tin plate manufacturers have some means for marking the differentially coated tin plate which would permit the can manufacturer to identify the light coated side or otherwise distinguish between the different sides. Various marking techniques of a mechanical, electrolytic, or chemical nature have been proposed for this purpose. One technique for marking the tin plate consists in the application to one side of the sheet intermediate the electroplating and flow brightening steps a suitable liquid reagent or marking material which is adapted to inhibit or interfere with subsequent flow brightening. This method is described in U.S. Patent No. 2,770,872 and is generally well known at this date to those skilled in the art. However, the success of the method in providing the desired dulling or marking effect depends to a large extent on the selection and utilization of an appropriate marking liquid.

One class of marking materials which is particularly effective comprises an aqueous solution containing an alkali metal silicate and a non-acidic salt of an alkaline metal, i.e. a salt of an alkali metal or an alkaline earth metal. Sodium silicate and potassium silicate are the preferred alkali metal silicates, and the non-acidic alkali metal or alkaline earth metal salt is preferably a sulfate, carbonate, nitrate or chromate of sodium, potassium, lithium, rubidium, cesium, calcium, barium, strontium, or magnesium. The alkali metal or alkaline earth metal salt must also be stable at the elevated temperature of the fusion or flow brightening step, i.e. the salt must be stable at a temperature somewhat above the fusion point of tin (450° F.). The desired marking or dulling can gener-

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ally be obtained by the action of the alkali metal or alkaline earth metal salt alone but the presence of the additional alkali metal silicate is highly desirable in order to prevent loss of the alkali metal or alkaline earth metal salt from the sheet by decrepitation and spalling during the fusion step. In other words, in the absence of the alkali metal silicate there is a tendency in some cases for the alkali metal or alkaline earth metal salt to become displaced or detached from the surface of the tin plate during the extremely rapid heating and evaporation of the aqueous marking solution which occurs prior to and during the fusion step.

In commercial practice, the fusion or flow brightening step is carried out using either an induction furnace, resistance heating means whereby the metal strip is heated internally by electric current, or a gas fired furnace wherein the fusion of the tin is accomplished by means of radiant heat from the gas burners. In a continuous electrolytic tinning line which may operate at speeds of from about 400 ft. per minute to about 800 ft. per minute it will be understood that the rate of evaporation of the marking solution in the flow brightening step is necessarily very rapid and as a result it has been observed that the dried salt residue on the sheet tends to decrepitate so that particles or crystals of the salt literally "pop off" from the strip and the desired marking or dulling effect is unsatisfactory. However, the presence of the alkali metal silicate in the aqueous marking solution overcomes this phenomenon, the silicate apparently acting as a binder between the dried particles of the marking salt and the tin coated base and also possibly effecting a more controlled and less explosive evaporation of water during the heating step.

For effective marking or dulling of the tin coated surface, the amount and concentration of the aqueous marking solution is regulated to provide at least 100 milligrams of the alkali metal or alkaline earth metal salt per square foot of treated surface. By way of example, the marking solution may contain from about 0.5 to about 10 grams of the alkali metal or alkaline earth metal salt per 100 cc. of solution and from about 0.75 to about 2 cc. of the alkali metal silicate per 100 cc. of solution. The preferred marking solution comprises sodium sulfate and sodium silicate.

The foregoing method of providing an identifying marking on tin plate is more fully described in Vincent P. Pearson et al. application Serial No. 561,353, filed January 25, 1956, and now U.S. Patent No. 2,876,176, to which reference may be made for additional details of the method.

In the manufacture of tin cans from tin plate soldering operations are employed to form side seams and for other purposes, and it is therefore important, especially in high speed automatic manufacturing techniques, that the tin plate possess good solderability characteristics. However, various factors will have an adverse effect on the solderability of tin plate, e.g. too much tin-iron alloy layer and too little free tin on the surface of the base metal sheet as the result of improper flow brightening conditions; foreign matter on the base metal as a result of improper pickling or cleaning; foreign matter on the tin coated surface as the result of improper handling of the tin plate, etc. Consequently, it is necessary that suitable precautions be taken during the manufacture of the tin plate at the steel mill and also during subsequent handling and fabrication thereof by the can manufacturer. When manufacturing tin cans from differentially coated tin plate which has been marked in accordance with the above described procedure using an aqueous silicate containing solution, frequent difficulties were encountered with poor solderability. After an ex-

tensive investigation of the problem I have found that poor solderability is attributable to the presence of a residual silicate film which apparently interferes with proper bonding or adhesion during the soldering operation. The present invention provides a method of eliminating this difficulty.

Accordingly, a broad object of the invention is to provide an improved process for the production of tin plate, particularly differentially coated tin plate having an identifying marking on one side thereof.

A further object of the invention is to provide a novel and improved process for the production of tin plate having satisfactory solderability characteristics.

Another object of the invention is to provide novel means for eliminating the detrimental effect of residual silicate on the solderability of differentially coated tin plate.

Other objects and advantages of the invention will be evident from the subsequent detailed description.

In a typical continuous electrolytic tinning line the steel strip passes first through a pickling tank for cleaning purposes and thence through one or more rinsing steps to insure removal of the acid or other pickle liquor from the strip. The strip then passes between a plurality of tin anodes in a plating tank containing an alkaline tin solution, the strip being the cathode. In the case of differentially coated tin plate, the current supplied to the respective anodes is regulated so as to obtain light and heavy deposits of tin on the respective sides of the strip. From the plating tank, the strip is passed through one or more rinsing steps for removal of the plating solution from the strip and is then dried. At this point in the line the marking solution is applied to one side of the strip following which the strip moves through the fusion or flow brightening furnace. Following the flow brightening step it is customary to provide one or more chemical or electrolytic treating steps for the purpose of removing oxide film or otherwise cleaning the strip and also for passivating the surface or otherwise protecting it against subsequent corrosion. For example, one technique which may be employed at this point is described in U.S. Patent No. 2,775,535 and consists in a cathodic treatment of the strip in an aqueous alkaline solution, e.g. sodium carbonate, followed by rinsing and a chromic acid dip. Other treatments well known in the art may also be employed at this point of the process. Finally, the strip is sheared to provide sheets of the desired size.

As heretofore described, it has been found that when the marking of the tin plate is effected by application of an aqueous solution containing a water soluble silicate, such as sodium or potassium silicate, the resultant tin plate frequently displays inferior solderability properties which are attributable to the presence on the marked or dulled side of the tin plate of a residual silicate film. In accordance with the present invention, I have found that this residual silicate can be effectively removed by contacting the marked side of the sheet with a dilute aqueous solution of a hydrofluoric acid. When the strip is so treated, the solderability characteristics are vastly improved.

In practicing the invention, the treatment with dilute aqueous hydrofluoric acid may be carried out at any convenient point following the fusion or flow brightening step. The removal of residual silicate by the hydrofluoric acid treatment has no detrimental effect on the marked or dulled surface. As previously explained, the primary function of the silicate is to insure adherence of the alkali metal or alkaline earth metal salt to the sheet during the fusion step and once this step has been completed, the subsequent removal of the silicate from the surface of the strip does not interfere in any way with the desired marked or dulled appearance.

Inasmuch as differentially coated tin plate is provided with a desired marking or dulled appearance on

only one side of the strip, it is only necessary to contact the marked or dulled side of the sheet with the aqueous hydrofluoric acid in order to accomplish the purpose of the invention. For example, this can be done by spraying or otherwise applying the aqueous hydrofluoric acid solution to only one side of the sheet. However, as a practical matter in the operation of a continuous line it will generally be desirable to pass the entire strip through a tank or vessel containing the dilute aqueous hydrofluoric acid bath. Such immersion of the strip in the hydrofluoric acid solution obviously results in contact of both the dulled and the bright sides of the sheet with the hydrofluoric acid. However, because of the fact that only a relatively dilute solution of hydrofluoric acid solution is employed and the contact time is relatively brief, no adverse effect is observed on the bright side of the strip and there is no measurable loss of tin by solution in the hydrofluoric acid.

As long as the aqueous solution of hydrofluoric acid is relatively dilute, the exact concentration is not critical. In general, the concentration of hydrofluoric acid is preferably from about 0.3% to about 3% by weight. To afford flexibility of operation, the tank containing the dilute hydrofluoric acid bath may be provided with a steam heating coil or other heating means for regulating the temperature of the bath. Preferably, the bath temperature should be from about 70° F. to about 100° F. but satisfactory results are usually obtained at prevailing room temperature. Because of the rapidity of the reaction of hydrofluoric acid with the silicate on the strip, the actual contact time in the bath may be very brief. For example, at the usual line speeds of from about 400 to about 800 feet per minute, the contact time may vary from about 1/2 to about 30 seconds.

In the case where the strip is subjected to chemical or electrolytic treatment following the fusion step for oxide removal or corrosion protection purposes, the location of the hydrofluoric acid treatment step may be varied to accommodate the requirements of the other treating steps. For example, in the two step treating sequence described briefly above wherein the strip receives a cathodic treatment in aqueous sodium carbonate followed by a chromic acid dip, the treatment with aqueous hydrofluoric acid may conveniently be interposed between the cathodic sodium carbonate treatment and the chromic acid dip. Thus, the strip as it emerges from the fusion furnace may be subjected to cathodic treatment in aqueous sodium carbonate and following a rinsing step may then be passed through the aqueous hydrofluoric acid bath. The strip is again rinsed to remove hydrofluoric acid and is finally passed through the chromic acid bath. Obviously, other slight variations in the sequence of operations following the fusion step may be employed to correlate with the other chemical or electrolytic treatments which are provided at the end of the line. In any event, following passage through the hydrofluoric acid bath the strip will always be rinsed in water or other fluid for removal of hydrofluoric acid.

To further illustrate the invention, the following specific example of a commercial operation is presented but it will be understood that the invention is not limited to the details of this example.

For the purpose of evaluating solderability of tin plate, a so-called capillary rise method was employed. In accordance with this method, a suitable tin plate sample is taken and is cut to provide a small elongated strip, e.g. approximately 3 inches by 1 inch. This strip is then bent or doubled upon itself until the two halves are spaced only a very slight distance apart, the spacing being regulated by using a jig and anvil to insure the same configuration and dimensions in successive samples. The bent sample is then immersed to a predetermined depth in molten solder for a fixed period and then removed and cooled. The bent or folded end of the sample is cut off and the two halves are pulled apart to reveal the extent

of rise of solder into the space between the strip halves. Using a scale, the capillary rise is measured to the nearest sixteenth of an inch. For acceptable solderability, tin plate having a coating weight of 0.25 lb. per base box should display a minimum capillary rise of $\frac{1}{16}$ inch (reported simply as 9), and tin plate having a coating weight of 0.75 lb. per base box should display a minimum capillary rise of $\frac{2}{16}$ inch (reported as 20).

Two comparative runs of approximately three months each were made on a commercial electrolytic tin plate line for producing differentially coated tin plate having a coating weight of 1 lb./base box on the heavy side and $\frac{1}{4}$ lb./base box on the light side. The strip was passed at a line speed of about 600 ft./min. successively through the following steps: pickling, plating, marking, flow brightening, cathodic cleaning in aqueous sodium carbonate, and a chromic acid dip. In one run an aqueous hydrofluoric acid dip was interposed between the cathodic cleaning and chromic acid dip, the conditions being otherwise the same. The base metal strip consisted of a flat-rolled, thin gauge, low carbon steel as commonly used in electrolytic tin plating.

The pickling step was carried out using an aqueous sulfuric acid bath (4 to 5% by volume) at a temperature of 150° F. to 170° F. The electrolytic tinning step was conducted in an aqueous alkaline sodium stannate solution containing 10-12 gm./liter of NaOH and 20-30 gm./liter of Sn at a temperature of 180° F. to 210° F. and with a current density of about 45 amperes/sq. ft. on the heavy side and about 30 amperes/sq. ft. on the light side. The marking of the light weight side of the strip was accomplished in accordance with the method described in Pearson et al. Pat. No. 2,876,176 using an aqueous solution of sodium sulfate (about 3% by wt.) and sodium silicate (about 0.8% by vol., 40° Bé.) which also contained about 0.1% by volume of a non-ionic surface active agent (polyoxyethylene ether). In the flow brightening step the strip was passed through a direct gas fired radiant heat furnace. The cathodic cleaning of the strip was conducted in an aqueous sodium carbonate bath (3-5 wt. percent) at a temperature of 160-170° F. and a current density of about 30 amperes/sq. ft. The aqueous chromic acid dip contained about .03 wt. percent CrO_3 partially neutralized with sodium carbonate and was employed at a temperature of 180-190° F.

In the run using HF treatment between the cathodic cleaning and chromic acid dip steps, an aqueous solution of HF (0.5-0.7 gm./liter) was employed at room temperature followed by a water rinse.

In the run without HF rinse a total of 338 test samples were taken at regular intervals and the average solderability, as determined by the capillary rise method described above, was 6. In the run with the HF rinse, a total of 309 samples were tested with an average solderability of 14. Thus, a substantial improvement in solderability was demonstrated in accordance with the invention.

Similar comparative tests were also made on a commercial electrolytic tin plate line of the character described above extending over a longer period. Average solderability determinations were calculated based on a minimum of 100 samples per month. Over an 8 month period using no HF treatment, the average monthly solderability ranged from 5 to 9 with an overall average for the entire period of 6.5. Immediately following this series, the HF treating step was incorporated in the line and the average monthly solderability over a period of 10 months ranged from 10 to 21 with an overall average for the entire period of 16.8.

I claim:

1. In the production of tin plate by electrolytically depositing tin on a base metal sheet, applying to a tin

coated surface of the sheet an aqueous solution adapted to inhibit subsequent flow brightening of the sheet and containing a water soluble silicate, and thereafter heating the sheet to an elevated temperature for fusing the electrodeposited tin and thereby flow brightening the sheet; the improvement which comprises contacting said surface of the sheet following the fusion step with a dilute aqueous solution of hydrofluoric acid whereby to remove residual silicate from the sheet and thereby improve the solderability of the tin plate, said hydrofluoric acid solution being sufficiently dilute and the contact time with the sheet being sufficiently brief to avoid any adverse effect on brightness and any substantial loss of tin.

2. The process of claim 1 further characterized in that said silicate comprises an alkali metal silicate.

3. The process of claim 1 further characterized in that said aqueous solution of hydrofluoric acid has a concentration of from about 0.3% to about 3% by weight.

4. The process of claim 3 further characterized in that the contacting with aqueous hydrofluoric acid solution is carried out at a temperature of from about 70° F. to about 100° F.

5. In the production of differentially coated tin plate by electrolytically depositing tin on a base metal sheet so that opposite sides of the sheet have relatively light and relatively heavy tin coatings, respectively, and subsequently heating the sheet to an elevated temperature for fusing the electrodeposited tin and thereby flow brightening the sheet wherein an identifying marking is provided on one side of the sheet by applying thereto intermediate the electrodeposition and fusion steps an aqueous solution adapted to inhibit flow brightening and containing a water soluble silicate; the improvement which comprises contacting the sheet following the fusion step with a dilute aqueous solution of hydrofluoric acid whereby to remove residual silicate from the sheet and thereby eliminate the detrimental effect of silicate on the solderability of the sheet, said hydrofluoric acid solution being sufficiently dilute and the contact time with the sheet being sufficiently brief to avoid any adverse effect on brightness and any substantial loss of tin.

6. The process of claim 5 further characterized in that said silicate comprises an alkali metal silicate and the contacting with aqueous hydrofluoric acid is carried out at a temperature of from about 70° F. to about 100° F. with a solution concentration of from about 0.3% to about 3% by weight of hydrofluoric acid.

7. In a process for producing tin plate including the successive steps of electrolytically depositing tin on a base metal sheet, applying to a tin coated surface of the sheet an aqueous silicate containing solution adapted to inhibit subsequent flow brightening, heating the sheet to an elevated temperature for fusing the electrodeposited tin, subjecting the sheet to cathodic treatment in aqueous alkaline medium, and finally applying aqueous chromic acid to the sheet; the improvement which comprises contacting said surface of the sheet, intermediate said cathodic treatment step and the application of chromic acid, with a dilute aqueous solution of hydrofluoric acid whereby to remove residual silicate from the sheet and thereby improve the solderability of the tin plate, said hydrofluoric acid solution being sufficiently dilute and the contact time with the sheet being sufficiently brief to avoid any adverse effect on brightness and any substantial loss of tin.

References Cited in the file of this patent

UNITED STATES PATENTS

2,770,872	Kadell	Nov. 20, 1956
2,775,535	Poole	Dec. 25, 1956
2,876,176	Pearson et al.	Mar. 3, 1959